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Impact of biodegradable polymers on agricultural soil health

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Abstract
In the last few decades, an interest has drawn in the use of biodegradable polymer materials in agriculture, medicine, packaging and other areas. For this reason, many researchers engaging their time and effort to synthesize novel polymer materials which are biodegradable and commercially viable as well as which will reduce the need for synthetic non-degradable polymers, thereby enhancing a positive effect both environmentally and economically. The development of biodegradable polymers has extensively contributed to soil health as well as industries related to agriculture by boosting up the effectiveness of fertilizers as well as the effectiveness of herbicides and pesticides by helping the controlled system which results in the use of lower doses. This review elucidates the opportunities along with the contribution to the sustainable agricultural practices with commercially viable by the applications of novel biodegradable polymers.

Keywords: Biodegradable polymer, bioaccumulation processes, slow-release fertilizer, controlled-release fertilizer, micronutrients, biosorption

Introduction
Synthetic polymers' invention opens a new horizon in the era of modern science and technology [1]. Today modern life is unimaginable without polymers. Many people consider the application of polymers as plastics use to make fibers, objects for household use and packaging purpose. But nowadays, polymers are essential in the areas of production, distribution and preparation of different products like kitchen applications, dentistry and in contact lenses, medical products for wound care, various equipment for protective purposes and leisure activities, sportswear & sporting materials, products for home & personal care and other many more areas.

Despite of all the advantages of plastics, which are not readily biodegradable, are being heavily discussed as materials responsible for detrimental effects on the environment. Since these materials are resistant to microbial degradation cause accumulation in the environment. The increasing impacts of fossil polymers' pollution on environment drew the attention to the necessity for the production of polymers which is biologically degradable from renewable sources as an alternative to these problems [2, 3]. Polymers, whether made from irrespectively renewable or synthetic sources, can degrade by the action of microorganisms [4, 5].

Biodegradation of polymers by the action of enzymes or chemicals occurs in two steps. The fragmentation of the polymers into smaller molecules of lower mass by abiotic reaction i.e. photo degradation, hydrolysis or oxidation, or by biotic reaction like degradation by microorganisms is the first step. The second step is the bio-assimilation of polymers fragments causes by microorganisms and their mineralization [6]. Such facts cause to promote the interest in biodegradable polymers in their extensive use in agriculture. Most recent research on the bespoke polymeric systems as well as the smart polymeric system [7] that is stimuli-responsive for different plant application has started. The continuous technological improvement of the using polymer materials contributes to the development of controlled delivery nutrients, agrochemicals, water management, soil conditioners, genetic engineering, and many more [8-10]. This review revealed the importance as well as optimism about the study of biodegradable polymers and their use and impact in agriculture.

Biodegradable polymers as agrochemical carriers
It is very important in agriculture to fulfill the plant's nutritional needs from macronutrients like Mg, Ca, N, K, P and S as well as micronutrients like Mn, Co, Cl, B, Fe, Cu, Zn, Mo

and Ni. Nevertheless, an adequate amount of those nutrients may not be present in the natural environment for plant's sufficient growth. For this reason, the use of agrochemicals becomes essential in agriculture as fertilizers, pesticides and herbicides. Besides this, as the knowledge about the lifetime of agrochemicals increase, the concern about unwanted environmental impacts such as the food chain's bioaccumulation processes and the potential hazard to neighboring ecosystem also increase, which become more relevant [11].

Fulfilling plants' nutritional needs without causing any contamination to the soil, the combined use of polymeric materials with agrochemicals has become an alternative instead of delivering agrochemicals directly into the soil [11]. Combination of polymers with agrochemicals could be defined as a chemical or physical process. For instance, controlling the release rate is physical while stabilizing the chemicals of polymer matrix is a chemical process. Selecting the best release system of active agents directed by their biological and chemical characteristics along with their physiochemical interactions. Besides this, the slow-release systems and the controlled release systems are the two classes. The slow-release fertilizer (SRF) delays its release by the mechanism of release characteristics, in comparison to the controlled-release fertilizer depending upon the type of the mechanism to liberate the nutrient into the environment [12]. The known factors that effect and controlled the rate of release as well as the pattern of controlled-release fertilizer (CRF) so that they can be controlled [13, 14]. To maintain food production along with minimizing environmental pollution with plant fertilizers, it is essential to improve nutrient recycling in agriculture.

A diverse polymer composition of a wide range has been used to fabricate agrochemical delivery devices for controlled release into the soil. In the Table 1 are listed some agrochemicals and polymers used for controlled and sustained release system.

Table 1: Some agrochemicals and polymers used for the controlled delivery of agrochemical

Agrochemical	Polymer
Urea	Polyethylene, polylactic acid, Chitosan, ethyl cellulose, polyhydroxybutyrate(phb)
NPK	Chitosan, cellulose, rosin, alkide resins, paraffins, polyolefines
$CaH_4P_2O_8$	Chitosan,
KH_2PO_4	Chitosan, gellan gum
KNO_3	Chitosan, Chitosan- clay, Xanthan
2,4,5-Trichloro-phenoxyacetates	Albumin
Validamycin($C_{20}H_{35}NO_{13}$)	Polystyrene, Polyacrylamides, polyamides

Interest focused on polymers in particular on those which consist of herbicides as pendent groups such as pentachlorophenol (PCP); 4 chloro-2-methylphenoxyacetic acid (CMPA) and 2,4-dichlorophenoxyacetic acid(2,4-D). Materials able to release herbicides as well as increase the retention of water in the sandy soil accompanying with the realizing of linking herbicides covalently to hydrophilic polymers. Oligooxyethylene methacrylates produce hydrogels by linking CMPA via ionic and covalent interaction.

Synthesizing of hydrophilic polymers by Akelah *et al*. and coworker by using different monomers of acrylates as cross-linking agents like diethylene glycol methacrylate (DEGMA), octaethylene glycol mathacrylate (OEGMA), acrylamide (AA), N, N-methylene bisacrylamide (MNBA), and tetraethylene glycol methacrylate (TEGMA) in 2,4-D and CMPA release [15]. A device proposed by the same authors characterized by poly (methylacrylic acid) with divinylbenzene (DVB) as crosslinker, derivatized by hexamethylene diamine, hydrazine, and ethylene diamine and then modify by the acid chlorides of 2,4-D and CMPA. One easy way of synthesizing polymers from diethyl-L-tartrate and diamines containing pendant hydroxyl groups was proposed by Akelah *et al*. [16]. Potentially bioactive and degradable polymers found by preparing in this way support their ability releasing herbicide 2,4-D into the soil. An increase in hydrophilicity of polymer increased the diffusion rate of the medium allowed the attack on bonding group. As increase the temperature and the pH of the surrounding medium of the polymers, increased the rate of the hydrolysis. Polyacrylamide derivatized based crossed linked gel with various diamides was tested by Kenawy *et al*. for realizing a slow release of chemically bonded 2,4-D [17].

The agrochemicals rate of release can effectively be tuned by changing different characteristics of polymers such as nature of the polymers namely ratio of hydrophilic/ hydrophobic, cross-linking amount, linear or branched nature and different non-covalent interactions like H-bonding, ionic interactions etc. The effect of comparatively small block content of polyethylene glycol (PEG) in poly(L-lactide-coglycolide)-poly(ethyleneglycol)-poly(L-lactide-co-glycolide) (PLGA-PEG-PLGA) compared to degradation of polymers and herbicide release was examined by Rychter *et al*. [18]. Their other findings were that even a short PEG block's presence in the chain of tarpolymer increased the polymers hydrophilicity, which increased the susceptibility of polymers to enzymatic and hydrolytic degradation in the environment of soil. A decreased degree of crystallinity occurred with the introduction of PEG block within PLGA-PEG-PLGA terpolymers which facilitated rapid biodegradation.

Varying the ratio of hydrophobic to hydrophilic segments and changing the crossed-linking density were tuned with the swelling pattern, biodegradability and capsulated 2,4-D herbicide release. At higher density of cross-linking and hydrophilicity, agrochemicals releasing rate desirable found low which results from less swelling and a slower rate of degradation. A significant effect can also on agrochemical release properties by cross-linkers nature. A study on preparing poly(acrylamide-co-itaconic acid) hydrogels cross-linked with either N,N'-methylene bis(acrylamide) (NMBA) or ethylene glycoldimethacrylate (EGDMA) revealed this result [19]. The authors revealed that the interaction of nitrate ions and pore size with certain sites provided by cross-linker permits both its retention and sustained and controlled release by calculating the controlled and sustained release of potassium nitrate fertilizer. A change in the crosslinker changes the balance of hydrophobic to hydrophilic ratio which in turn affects the swelling of hydrogels and the rate of release. It was observed that the higher swelling and rapid release rate were found for more hydrophilic EGDMA cross-linked hydrogels than the NMBA cross-linked gels. It revealed from the same experiment that the swelling behavior in saline solution affected by the EGDMA cross-linker polymer because of ionic interactions with the EGDM moiety, on the other hand, the effect on the NMBA cross-linker polymer was negligible.

Adak *et al*. [20] reported on the synthesizing of a number of amphiphilic co-polymer micelles as a series from PEG-b-poly(aliphatic acid) for the controlled and sustained release of imidacloprid. PEG 300, 600, and 1000 had chosen as the hydrophilic moieties, and different aliphatic diacids such as adipic acid, glutaric acid, suberic acid, and pimelic acid were used as the hydrophobic head group. The investigation of the effect of the chain length of PEG and the hydrophobic head group's nature was carried out on the critical aggregation constant, imidacloprid encapsulation efficiency, micelles size and rate of release. A slower release rate for imidacloprid from these micelles(size-170-250nm) than of the commercially available formulation was found; nevertheless, not any uniform trend was found for the polymers containing different hydrophilic segments. The same pesticide was also encapsulated into 5-10µm sized particles composed of an amphiphilic diblock polymer poly(lactic-co-glycolic acid) [21]. It was revealed that the required imidacloprid concentration was 200 times lower than that for commercially formulations when using such functional micro dispensers against crop pests. Preparing agrochemical delivery systems utilizes amphiphilic diblock polymers along with triblock copolymers.

Heavy metal removal from water and soils

Metal ions are of three categories: some are toxic, such as Hg, Cr, Pb, Cu, Zn, Ni, Cd, As, Co, and Sn; some are precious metals, e.g., Pd, Pt, Ag, Au & Ru; and the rest are radioactive e.g., U, Th, Ra, and Am [22]. Among these metals, some metal ions combined with agrochemicals as the form of fertilizer, insecticides and herbicides, prior to release into the soil. The soil itself is the source of nutrients for plants and living organisms without the addition of agrochemicals. Therefore, some metal ions although trace amounts present naturally in the soil can function as necessary micronutrients for living organism. All these metal ions are of three categories: essential micronutrients (Fe, Zn, Mn, Na, Ca, K, Cu, and Mo), beneficial micronutrients (Co, Ni, and V), and non-essential micronutrients (Cd, Cr, Hg, and Pb). Huge amount of agrochemicals is being used to increase profit and productivity in an abusive manner daily in agriculture. As a result, large amount of agricultural toxic contaminants is piling up daily into soil, ponds, rivers and also ground water such as organic, inorganic and metal ions. The cumulative effect and naturally non-degradable character of these metal ions are threatening problems for the environment. Hence, the toxicity of these metal ions can cause severe ecological damage and the use of contaminated food and water can harm to humans and other animals enormously [23]. Thus scientists are engaging time to develop techniques concerning over soil and water pollution that are aimed to mitigate ecological harm that are already threatened.

Furthermore, waste solution contains huge amount of various ions which are harmful and hazardous to the environment. Selective decontamination of effluent streams is one of the ways to use polymeric ion exchange resins replacing undesirable ion that caused no harm to environment [24]. Usually, polymeric ion-exchange resins are versatile materials on the basis of cross linked polymers that have different types of geometric pore [25]. By the copolymerization or chemical transformation reaction, polymer can be formed using appropriate common crosslinking agents divinylbenzene and ethylene glycol dimethacrylate (EGDMA) [26] while surface functionality can be increased by using co-monomers of desired functional groups. Styrene [27] are the most common functional groups related materials responsible for the interaction with the metal ions and have weakly acidic or basic functionalities for the preparation of this kind of material. Kocaoba *et al*. [28] used acrylic acid based resin for Cr(III) removal, acrylamide(AAm) based hydrogel is used in Pb (II), Hg (II), Cd (II) and Cr (VI) removal [29, 30] and amine resins for Cr (VI) [31], Ni (II), Zn (II), Cu (II), Cd (II) and Pb (II) [32]. Several articles revealed that sulfonate groups and phosphoric groups are the other versatile functionalitie [33, 34]; finally, thiacrown polymers stick on polystyrene-divinyl-benzene were used for Hg (II) removal [35].

Studying all most literature, it might be noticed that the number of articles that located some methods for the removal of heavy metal in aqueous environments is abundant with comparison to the number of publications that only for the techniques for decontamination of soils.

Recovery method for contaminated areas involves polymeric biosorption: Microbial biomass' characteristic biosorption is the biological process in which biomimetic-type techniques bind heavy metals defined as biosorption has been adopted even from very dilute solutions. Biosorption has been studies both in water and soil system as an alternative technique of bioremediation to metal ions removal. By this techniques, either inorganic or organic pollutants could be removed through ion exchange. Research results revealed that the sorption capacity is high and the cost of this method is low [36]. The common use of polymers other than biosorption has also as toxic elements' sorbent materials arising from agrochemicals as a way of water's as well as soil's decontamination. For a better understanding of the polymer's sorption mechanism, first of all, it is necessary to identify the functional groups present in the material. On the surface of the polymeric material, due to the chemical affinity of certain functional groups, metal ions are absorbed [37].

The most common group of polymers such as cellulose, chitin, chitosan, exobiopolymers and some other polysaccharides are applied for metal sorption because of their ionizable carboxylic acid, amine, amide and alcohol functional groups for ionic bonding [38]. Besides this, some fiber extracted from natural sources such as sugarcane bagasse, green coconut fiber and bamboo fiber, etc. has also been applied as biosorbent. The main advantage of these are the easy and low-cost recovery from industrial and/or agricultural residue materials. These crude fibers which consist of acidic groups responsible for metal ions sorption are mainly composed of cellulose and hemicellulose.

Exopolymer films were tasted by Pal and Paul [39] in turn of contaminated water's remediation process. Expolymer biofilms are the extracellular substances of microorganism's origin capable of absorbing metal ions by electrostatic interaction. Their results revealed that some metals were absorbed most efficiently such as zinc, copper, chromium, cobalt, nickel and CrO. Metallic ions removal methods such as filtration, electrochemical treatment, chemical precipitation, membrane technologies, ion exchange, and adsorption over active coal in aqueous environments have thus far been based on biological treatments [39]. In several regions from Brazil, due to its abundance, agricultural residues like this including sugarcane bagasse have gained much attention to apply in this field. It was observed from different research that the most commonly used metal ion ‘sequestrant” ís cellulose among the materials used as biosorbents due to the abundant surface hydroxyl groups of cellulose which could functionalize to contain more polar or ionizable pendant groups to enhance ion exchange for decontaminating water.

The applications of super absorbent polymers in soil

Many regions of the world, water scarcity and desertification are severe problems because they interrupt agricultural development. Desertification is a process of land degradation by which a fertile land changes itself in arid, semiarid and dry areas. This can be caused by various factors including climate changes, drought, deforestation, improper agriculture, human activities. These problems can be reduced using synthetic materials which have good water absorption and retention capability even at high temperature. Superabsorbent polymers (SAPs’) have excellent water absorbency and water retention properties. SAPs’ can be used to diminish these problems because, SAPs are very well known and already used in various hygienic napkins, drug delivery systems, agricultural applications, sensors and disposable diapers like uses. Encouraging results have been found from their use for agricultural applications; as they reduce water consumption in irrigation, increase the rate of plant growth with fertilizer retention in the soil and reduce the death rate of plants. Recent study has been carried out for the modification of superabsorbent co-polymers in order to enhancing the rate of absorption, gel strength and their absorbency.

Raju *et al*. [40] formulated a series of superabsorbent co-polymers from some monomers like potassium methacrylate (KMA), 2-hydroxyethylmethacrylate (HEMA) and acrylamide (Am) and they were using N, N-methylene-bis-acrylamide (MNBA) as crosslinking agent. Studies were carried out on the influencing synthetic parameters like the concentration of the monomer, concentration of initiator and concentration of crosslinker. It was observed from the results of experiments that the superabsorbents showed very good absorbency and rapid swelling capacity both in water and NaCl solution. It was also observed from the experiment that the water retention capacity of the soil, germination power of ground nut seeds and the growth of plants increased to a great extent. SAPs showed considerable attention as release formulation, the combination of fertilizer(nutrient) with SAPs can supply nutrient with slow and controlled release to the plants and at the same time it can help for soil conditioning by minimizing the frequency and amounts of irrigation. It is mentioned by Zhan *et al*. [41] that the material found from the synthesis of SAPs by the reaction of polyvinyl alcohol with phosphoric acid, showed the ability to absorbed and retain water. It also provides phosphate as nutrient to the plants as controlled release rate. The polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid, collagen with acrylic acid prepare a phosphorus loaded smart SAP material [42] can release fertilizer to the plants with slow and controlled rate.

The chelation of iron caused additional non-covalent cross-linking when obtained polymer coordinated with Fe (III), which increase the controlled release characteristics of the phosphorus fertilizer loaded polymer but reduce the water absorption quality. XU *et al*. [43] prepared an interesting and effective high salt tolerance and pH sensitive SAPs by grafting zwitterionic groups on to the polymer backbone. Especially, their efforts were to prepare amphoteric SAPs by grafting acrylic acid onto the backbone of natural polymer collagen with dimethyl-di-allyl-ammonium chloride (DMDAAC) as crosslinking agent. This SAP revealed reversible swelling property along with pH dependency and responsive herbicide release characteristics. All these reports focus the ability of SAPs to improve efficiently soil water retention [47], soil condition [45, 46] and water use efficiency. Moreover, in the primary stage of the growth of plants, the rate of carbon fixation and the utilization capacity of granular fertilizer [43] may also be flourished. It is apparent from the literature review that inclusion of the groups (i.e., -COOH, -SO_3H, -NH_2, -OH) improve SAP water capacity, whereas to enhance the salt resistance, zwitter ionic groups are very effective.

Conclusions

The high demand of agricultural products for the global population, it is necessary to improve the quality of the soil for agricultural production. Consequently, many agrochemicals i.e., fertilizer and pesticides are being used for agricultural production. Using new technology and materials contributed to improving the soil conditions, nutrients, and water management. Biodegradable polymers have numerous versatile mechanical and chemical properties that satisfy specific requirements. Without contamination of soil, various polymers can be used as carriers for agrochemicals in order to deliver active components directly to plants with a controlled release rate. The use of biodegradable polymers in agriculture would be eco-friendlier and economically sustainable with high yield of crops.

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